

RESERVE COPY.

PATENT SPECIFICATION

743,842



Date of Application and filing Complete Specification March 17, 1952.

No. 6815/52.

Application made in United States of America on March 16, 1951.

Complete Specification Published Jan. 25, 1956.

Index at acceptance: —Classes 2(3), C3A10A3, C3A10A4(E:F), C3(A10A5A1:C10:X); 2(5), P10C(12B:18), P10C20D(1:3), P10D1A; 91, F1, G1A1; and 95, A2.

COMPLETE SPECIFICATION

Improvements in or relating to Basic Salts or Soaps

We, ANGLAMOL LIMITED, of 110, Strand, London, W.C.2, a Company registered under the laws of Great Britain, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

(1) This invention relates to new compositions of matter, and more particularly pertains to novel organic salt complexes and novel methods of producing same.

It is now well known that when preparing a salt or soap of an organic acid, the mere use of an excess of neutralizing agent, which in the prior art has been in the form of an oxide, hydroxide, carbonate, etc., of a desired metal, results in a product which contains an amount of metal in excess of that theoretically required to replace the acidic hydrogens of the organic acid used as a starting material.

Work with this type of product has shown that for many uses, particularly where extreme care must be exercised to prevent the composition from being corrosive, as for example, in lubricants, desirable results are secured by the use of these so-called basic salts or soaps.

Among the earlier workers in the art who recognized this factor and indicated that the use of basic soaps was desirable was Bergstrom, who in his U.S. Patents, No's. 2,270,577 and 2,279,086, made reference to the desirability of using the basic soap without, however, giving any specific method for the preparation of such soaps. A similar disclosure is found in vanEss, U.S. Patent No. 2,372,411.

With the demonstrated superiority of such basic soaps over the normal or slightly acid soaps, the prior art workers then attempted to find ways of increasing the basicity of the soaps, or stated another way, increasing the amount of salt-forming radical or metal, for example, held in

stable form in what was termed as a metal complex. One of the earliest patents referring to these basic salts as complexes or co-ordination compounds is McNab U.S. Patent No. 2,418,894, who gives no indication in his patent as to the molecular structure of the product. As might be expected, one of the first steps employed to produce a metal salt having an intended large excess of metal in combination was to use an unusually large excess of neutralizing agent such as lime. A representative patent disclosing this procedure is Griesinger *et al*, U.S. Patent No. 2,402,325, which suggested the use of a neutralizing agent up to 220% of the theoretical amount. This large excess of neutralizing agent was employed in a process more or less conventional for producing salts or soaps excepting that the process was carried out in the presence of steam in order to facilitate the formation of the end product.

The work of Griesinger was followed by the work of Campbell and Dellinger as given in U.S. Patent No. 2,485,861. These patentees base their disclosure on the hypothesis that minor amounts of an alkaline earth metal hydroxide or carbonate can be peptized or held in a state of colloidal suspension in oil by means of an oil-soluble mahogany sulphonate. Another worker in the art who sought to combine in such complexes an excess of metal was Mertes, whose U.S. Patent No. 2,501,731 was granted March 28, 1950. Mertes first prepared the normal soap and stated that such soap or soap concentrate "may have additional base combined therewith by a more or less simple mixing and heating operation followed by filtering." The disclosure in Mertes appears to indicate that his product is similar to that of Campbell and Dellinger, in that, the excess neutralizing agent was held in the product in the form of a colloidal suspension.

In all of the prior art processes, the

procedure for obtaining the so-called basic soaps is essentially the same, and it was found that the amount of salt forming radical or metal which can be combined in the basic soap, while high, according to previous standards, nevertheless could be improved upon as to the salt-forming radical content. Now, therefore, it is the purpose of this invention to provide novel methods of producing novel salt complexes which contain more salt-forming radicals in combination than was heretofore possible.

By means of the present invention, it is now possible to obtain organic salt complexes which contain more cationic salt-forming radicals or higher salt-forming radical ratios than is possible by prior art processes. With regard to lubricants, these high cationic salt-forming radical-containing complexes are for example particularly suited as detergents, and by reason of the salt-forming radical or e.g., metal concentration can be used in amounts appreciably less than other additives known in the prior art in order to attain a desired level of performance. It will also be observed that by virtue of the more effective nature of the present complexes in lubricants, usually it will cost less to obtain a desired result, because appreciably less additive is required. The organic salt complexes are produced in accordance with the present invention as a fluid, which is readily adapted for application where high concentrations of cationic salt-forming radicals are desired. For example, if the complex alone is desired, it can be produced in mineral oil solutions of at least 20% concentrations; whereas if the complex is wanted in combination with other additives, it can be available in concentrations of at least about 10% in mineral oils.

An object of the present invention is to provide novel salt complexes. Another object of the present invention is to provide new methods of producing novel salt complexes. A further object of the present invention is to provide novel salt complexes which are especially adapted for use in lubricants. Other objects or advantages of this invention will be apparent from the following explanation and description thereof:—

Essentially the present invention comprises the preparation of novel salt complexes formed with an oil-soluble acidic organic compound and/or the salt thereof; a material which is hereinafter referred to as the promoter; salts or bases; and water.

Another aspect of the present invention involves the preparation of salt

complexes comprising an oil-soluble salt of an acidic organic compound having in complex formation therewith a salt or base, and said complex contains a higher salt-forming radical content than is heretofore known.

Still another aspect of the present invention is to treat the salt complexes mentioned above with a material which will possess acid characteristics in the process mass so as to adjust the alkalinity of the salt complex and/or to partially or substantially completely recover the promoter in the ionizable form.

More particularly, the present invention is concerned with salt complexes having a metal ratio greater than 2:2 which are prepared by the method comprising:—

- I. Preparing and mixing a mass in which, at 50° C. at least 50% of the components are in a liquid state, and in which mass the active components consist of:—
 - (i) oil-soluble compounds selected from the class consisting of:—
 - (1) acidic organic compounds; and
 - (2) salts of acidic organic compounds; and
 - (3) mixtures of (1) and (2).
 - (ii) phenolic compounds other than those selected as components (i) selected from the class consisting of:—
 - (1) compounds having the formula AH , in which A is an anionic radical, and H is hydrogen, which compounds:—
 - (a) are water-soluble at a temperature of 50° C. to the extent of at least 0.0005%; and
 - (b) in the presence of water, have an ionization constant greater than about 1×10^{-10} at about 25° C. and the saturated aqueous solutions of which at about 25° C. have pH values no greater than 7.0;
 - (2) the metal salts of the compounds defined by (1) above; the relative amounts of (i) and (ii) used being in the range of from about one equivalent of (i) to about ten equivalents of (ii) to about one equivalent of (i) to about one equivalent of (ii);
 - (iii) compounds other than those selected as components (i) and (ii) selected from the class consisting of:—
 - (1) salts; and
 - (2) bases;
 in an amount such that there are present in the mass a total of substantially more than one equivalent

lent of metal salt-forming radicals, including those present in components (i) and (ii), per equivalent of (i) plus (ii); and

5 (iv) materials selected from the class consisting of:—

(1) water;

(2) the water-soluble alcohols and mixtures of such alcohols, and

10 (3) mixtures of water and such alcohols

in an amount, inclusive of that in chemical combination with all of the components present, equal to at least one mole per mole of (ii).

15

II. and then maintaining the mass at a temperature and for a period of time sufficient to drive off substantially any free water and alcohol, including water

20 of hydration, which may be present.

In an alternative aspect the present invention is concerned with salt complexes having a metal ratio greater than 2.2 which are prepared by the method

25 comprising:—

I. Preparing and mixing a mass in which, at 50° C., at least 50% of the components are in the liquid state and in which mass the active components consist

30 of:—

(i) oil-soluble compounds selected from the class consisting of:—

(1) acidic organic compounds;

(2) salts of acidic organic compounds, and

(3) mixtures of (1) and (2).

(ii) compounds other than those selected as component (i) containing element selected from the class consisting of oxygen and sulphur, which compounds are selected from the class consisting of:—

(1) compounds having the formula AH_n , in which A is an anionic radical, and H is hydrogen, and which:—

(a) are water-soluble at a temperature of 50° C. to the extent of at least .0005%; and

(b) in the presence of water, have an ionization constant greater than about 1×10^{-10} at about 25° C. and the saturated aqueous solutions of which at about 25° C. have pH values not greater than 7.0; and which compounds are selected from the class consisting of:—

(a¹) organic compounds;

(b¹) inorganic compounds containing a plurality of atoms of an acid-forming element;

(2) The metallic salts of (1) above; the relative amounts of (i) and (ii) used being in the range of from about one equivalent of (i) to about ten equivalents of (ii), to about ten equivalents of (i) to about one equivalent of (ii);

(iii) compounds other than those selected as components (i) and (ii) selected from the class consisting of:—

(1) salts; and

(2) bases;

in an amount such that there are present in the mass a total of substantially more than one equivalent of metal salt-forming radicals, including those present in components (i) and (ii), per equivalent of (i) plus (ii); and

(iv) materials selected from the class consisting of:—

(1) water;

(2) the water-soluble alcohols and mixtures of such alcohols, and

(3) mixtures of water and such alcohols

in an amount, inclusive of that in chemical combination with all of the components present, equal to at least one mole per mole of (iii);

II. and then maintaining the mass at a temperature and for a period of time sufficient to drive off substantially all free water and alcohol including water of hydration, which may be present.

III. Treating the mass with sufficient amounts of a material which in the presence of the mass will form a material having a higher ionization constant than AH, to liberate in the form of AH, a substantial portion of the radical A originally present in (ii).

If desired, the above salt complexes prepared in accordance with Step III can then undergo treatment to remove from the mass so much of AH as may have been formed by Step III.

As described above, the inorganic promoter is a compound "containing a plurality of atoms of an acid-forming element". However, it should be understood for the purposes of this invention that the above description of the inorganic promoter includes those compounds containing a plurality of atoms of an element capable of forming acids either in combination with hydrogen alone or in combination with hydrogen and oxygen. Further, for the present invention those inorganic promoters which contain a non-metallic acid-forming element are preferred.

THE OIL SOLUBLE ACIDIC ORGANIC
COMPOUNDS AND/OR THE SALTS THEREOF

The oil-soluble acidic organic compounds and/or the salts thereof employed for the purposes of the present invention include a variety of classes of compounds, such as the aliphatic or aromatic organic acids, e.g., the sulfur acids, the carboxylic acids, acids of phosphorous, or the salts of such acids, including the corresponding thio acids of any of the foregoing as well as mixtures of the same. The aromatic compounds include the mono- or polynuclear types of the benzoid and heterocyclic classes; whereas the aliphatic compounds are for example, the acyclic and cycloaliphatic compounds. It is intended that all such compounds be oil soluble for this invention, and in the preferred instance "oil solubility" is meant that the salt of the acidic organic compound will possess a solubility of at least about 10% in Pennsylvania conventionally refined mineral oil having a viscosity of about 150 SUS at 100° F., or what is commonly known as Pennsylvania 150 neutral oil.

More specific illustrations of the type of oil-soluble acidic organic compounds or the salts thereof which can be employed are, for example:—

- (1) organic acids in which:—
 - (a) sulfur is the acid-forming element, for example:—
 - organic acids containing the $\text{—SO}_3\text{H}$ radical, e.g.:—
 - sulfonic acids
 - sulfamic acids
 - thiosulfonic acids
 - organic acids containing the $\text{—SO}_2\text{H}$ radical, e.g.:—
 - sulfinic acids
 - thionamic acids
 - sulfenic acids
 - partial esters of polybasic inorganic sulfur acids, e.g.:—
 - mono-esters of sulfuric acid
 - mono-esters of sulfurous acid
 - mono-esters of thiosulfuric acid
 - (b) selenium is the acid-forming element, for example:—
 - selenonic acids
 - seleninic acids
 - partial esters of polybasic inorganic selenium acids, e.g.:—
 - mono-esters of selenic acid
 - mono-esters of selenous acid
 - (c) tellurium is the acid-forming element, for example:—
 - telluronic acids
 - tellurinic acids
 - partial esters of polybasic

inorganic tellurium acids, e.g.:—

mono-esters of telluric acid
mono-esters of tellurous acid

(d) carbon is the acid-forming element, for example:—

organic acids containing the $\text{—CO}_2\text{H}$ radical, e.g.:—

carboxylic acids

N-substituted carbamic acid

organic acids containing the $\text{—CX}_2\text{H}$ radical, where X is either O or S and at least one

X is sulfur, e.g.:—

thiocarboxylic acids

N-substituted thiocarbamic acid

seleno-carboxylic acids

telluro-carboxylic acids

(e) nitrogen is the acid-forming element, for example:—

nitrolic acids:

$\text{R—C}(\text{:NOH})\text{NO}_2$

nitrosolic acids:

$\text{R—C}(\text{:NOH})\text{NO}$

nitronic acids: $\text{R}_2\text{C}:\text{NOOH}$

nitroic acids: $\text{RNO}(\text{OH})_2$

carbazylic acids:

$\text{R—C}(\text{:NH})\text{NH}_2$

(f) phosphorus is the acid-forming element, for example:—

phosphonous or phosphinous acids; $\text{R}_x\text{P}(\text{OH})_{3-x}$ where x is 1 or 2

phosphonic or phosphinic acids; $\text{R}_x\text{PO}(\text{OH})_{3-x}$ where x is 1 or 2

thiophosphonous or thiophosphinous acids; $\text{R}_x\text{P}(\text{ZH})_{3-x}$ where x is 1 or 2, and

where Z is either O or S and at least one Z is sulfur

thiophosphonic or thiophosphinic acids; $\text{R}_x\text{PZ}(\text{ZH})_{3-x}$ where x is 1 or 2, and where Z is either O or S and at least one

Z is sulfur

partial esters of polybasic inorganic phosphorus acids, for example:—

mono-esters of phosphorus acid

mono-esters of thiophosphorus acids

mono- and di-esters of phosphoric acid

mono- and di-esters of thiophosphoric acids

partial esters of pyrophosphoric acid

partial esters of pyrophosphorous acid

partial esters of polyphosphoric acids

130

- partial esters of polyphosphorous acids
 partial esters of pyrothiophosphoric acids
 partial esters of pyrothiophosphorous acids
 partial esters of thiopolyphosphoric acids
 partial esters of thiopolyphosphorous acids
 (g) arsenic is the acid-forming element, for example:—
 arsinic acids
 arsonic acids
 partial esters of polybasic, inorganic, arsenic-derived acids, e.g.:—
 mono-esters of arsenious acid
 mono- and di-esters of arsenic acid
 (h) antimony is the acid-forming element, for example:—
 stibonic acids
 partial esters of polybasic inorganic antimony acids, e.g.:—
 mono-esters of antimonous acid
 mono- and di-esters of antimonic acid
 (i) silicon is the acid-forming element, for example:—
 silicic acids: RSiOOH
 partial esters of silicic acid
 (j) tin is the acid-forming element, for example:—
 stannonic acids; RSnOOH
 (k) lead is the acid-forming element, for example:—
 plumbonic acids; $\text{R}_2\text{Pb(OH)}_2$
 RPbOOH
- (2) metal salts of the organic acids listed under (1).
- 45 The metal salts include the mono or polyvalent metals, such as the light or heavy metals, or the alkali and alkaline earth metals such as sodium, lithium, potassium, calcium, barium, strontium, magnesium, and other specific examples, are zinc, cadmium, mercury, lead, tin, iron, cobalt, copper, manganese, aluminium, chromium, nickel.
- The following list of compounds serve to more specifically illustrate the types of acidic organic compounds which are contemplated for this invention. However, it should be understood that for every acidic organic compound enumerated, a corresponding specific metal or organic salt of the types discussed above and illustrated below are intended.
- 30 mahogany sulfonic acids
 petrolatum sulfonic acids
- substituted aromatic sulfonic acids 65
 e.g.:—
 mono- and poly-wax substituted naphthalene sulfonic acids
 mono- and poly-wax substituted phenol sulfonic acids 70
 mono- and poly-wax substituted diphenyl ether sulfonic acids
 mono- and poly-wax substituted naphthalene disulfide sulfonic acids
 mono- and poly-wax substituted diphenyl amine sulfonic acids 75
 mono- and poly-wax substituted thiophene sulfonic acids
 mono- and poly-wax substituted alpha-chloronaphthalene sulfonic acids 80
 N,N-di-wax aniline sulfonic acids
 fuel oil substituted naphthalene sulfonic acids
 fuel oil substituted diphenyl ether sulfonic acids 85
 kerosene substituted diphenyl ether sulfonic acids
 petrolatum substituted naphthalene sulfonic acids 90
 petrolatum substituted phenol sulfonic acids
 petrolatum substituted anthracene sulfonic acids
 petrolatum substituted naphthalene disulfide sulfonic acids 95
 ceryl-diphenylene sulfonic acids
 cetyl chloro-benzene sulfonic acids
 cetyl-phenol sulfonic acids
 cetyl-phenol disulfide sulfonic acids 100
 cetyl-phenol monosulfide sulfonic acids
 di-cetyl thianthrene sulfonic acids
 cetoxyl capryl benzene sulfonic acids 105
 di-lauryl chlorophenol sulfonic acids
 di-lauryl beta-naphthol sulfonic acids
 tri-lauryl phenothioxine sulfonic acids 110
 di-lauryl mono-chloro diphenyl ether sulfonic acids
 bis-(di-isobutyl-carbinyl) naphthalene sulfonic acids
 di-capryl nitro-naphthalene sulfonic acids 115
 tri-capryl benzene sulfonic acids
 tri-capryl diphenyl sulfide sulfonic acids
 di-capryl methyl naphthalene sulfonic acids 120
 di-capryl ortho-phenylphenol sulfonic acids
 tetra-capryl meta-terphenyl
 di-capryl thiophene sulfonic acids 125
 diisobutyl (2,4,5-trichlorobenzyloxy) benzene sulfonic acids
 p-capryl-o-cyclohexyl phenol sulfonic acids

- bis-(diisobutyl)naphthalene sulfonic acids
 tris-(diisobutyl) anthracene sulfonic acids
 6 bis-(diisobutyl)diphenylene sulfide sulfonic acids
 Aliphatic sulfonic acids (acyclic), e.g.:—
 10 paraffin wax sulfonic acids
 unsaturated paraffin wax sulfonic acids
 hydroxyl-substituted paraffin wax sulfonic acids
 nitroso-substituted paraffin wax sulfonic acids
 15 chloro-substituted paraffin wax sulfonic acids
 unsaturated sulfonic acids derived from polyalkylenes containing at least 15 carbon atoms, e.g.:—
 20 tetraisobutylene sulfonic acids
 tetra-amylene sulfonic acids
 Cycloaliphatic sulfonic acids e.g.:—
 petroleum naphthene sulfonic acids
 25 cetyl-cyclopentyl sulfonic acids
 lauryl-cyclohexyl sulfonic acids
 bis-(diisobutyl) cyclohexyl sulfonic acids
 mono- and poly-wax substituted cyclohexyl sulfonic acids
 30

While the above compounds and classes thereof are useful for the purposes of this invention, it should be understood that they are not all equivalent, but that 35 under certain conditions some are more desirable or effective than others.

THE PROMOTER

The compound employed for the purposes hereunder can be represented by the 40 formula AH, in which A is an anionic radical and H is hydrogen and/or the salt thereof. The compounds AH have a water solubility at a temperature of 50° C. to the extent of at least about 0.0005% and 45 will, in the presence of water at about 25° C., have an ionization constant greater than about 1×10^{-10} as well as have a pH value not greater than 7 at about 25° C. when employed in saturated 50 aqueous solutions.

The promoter AH can be organic or inorganic. In the case of the inorganic promoter it is intended to include only those which contain a plurality of atoms of an 55 acid-forming element which are capable of forming acids either in combination with hydrogen alone or in combination with hydrogen and oxygen. It is preferred to use those promoters in which the acid-forming element is non-metallic. 60

With respect to the organic promoter AH, a particular subclass thereof includes the compounds AXH in which A and H are defined as given above, and X is either

oxygen or sulfur. More particularly, as 65 for the organic promoters, it is preferred to employ the salts of compounds AH which have oil solubility of less than 10% in a conventionally refined solvent extracted Pennsylvania oil having a 150 70 SUS @ 100° F., commonly referred to as Pennsylvania 150 neutral oil.

SALTS AND BASES (THE BASING MATERIAL)

The salt or base employed furnishes the 75 cationic salt-forming radical to the desired salt complex. These salts or bases should preferably have a water solubility of at least about 0.0003% to 50° C., and still more preferred are "basic" com- 80 pounds, i.e., those compounds which give an alkaline reaction or pH value greater than 7 in aqueous solutions.

Generically the salts or bases can be represented by the structural formula MX 85 wherein M is a metal radical and X is an anionic radical.

It should be understood that all salts or bases are not equivalent for this invention, because under certain conditions 90 some are more desirable or effective than others.

The formation of the salt complex is accomplished with water or an alcohol or mixtures of both. The water is present as 95 a result of addition to the mixture, or is liberated from compounds incorporated into the mixture as a result of being subjected to processing temperatures. It is preferred to employ water which is added 10 to the mixture.

The alcohol employed can be either monohydric or polyhydric, and should preferably be at least about 5% water soluble @ 15° C. Examples 10 of monohydric alcohols are methanol, ethanol, propanol-1, propanol-2, butanol-1, butanol-2, isobutyl alcohol, *t*-butyl alcohol, pentanol-3, and examples of polyhydric alcohols are ethylene glycol, 15 propylene glycol, butylene glycol, amyleneglycol, hexylene glycol, pentaerythritol.

Water and alcohol can be used together in effecting the formation of the salt com- 1. plex. Ordinarily mixtures of the same in any relative proportion are useful; however it is preferred to employ mixtures containing at least 60% water.

THE ACIDIC MATERIAL

As previously indicated, one form of the process of the present invention includes the step of treating the immediate product with an acidic material for the purpose of liberating therefrom at 1 least a portion of the material previously referred to as the promoter. A particu-

larly effective acidic material which has been utilized for this purpose is carbon dioxide. We are aware of the fact that Mertes in his above-identified U.S. Patent No. 2,501,731 suggested transforming a sodium hydroxide-calcium sulphonate complex into the sodium carbonate-calcium sulphonate complex or the corresponding bicarbonate complex by blowing the hydroxide complex with carbon dioxide at elevated temperatures.

In our process, the step of treating with an acidic material such as carbon dioxide or even with air has the effect of liberating from the immediate product formed a part at least of the anionic radical of the compound used as the promoter material. Thus the presence in the immediate product of the promoter material, in combined form, clearly distinguishes the immediate product from any organic salt complex type material heretofore produced. Moreover, the nature of the product formed by regenerating from the immediate product at least a portion of the anionic radical of the promoter material leaves that product with a composition which is quite different from prior art organic complexes. It is recognized that in accordance with the present invention, the salt form of promoter can be employed in forming the salt complex. However, notwithstanding this fact, upon treating the salt complex with the acidic material to be more particularly defined below, this salt compound is released or liberated from association in the salt complex as the ionizable compound and not the salt.

The acidic material employed for this purpose can be either a liquid, gas, or solid just so long as the material when present in the mass containing the salt complex will possess an ionization constant greater than the promoter which is released or liberated from association in the salt complex. Thus, for the purpose of this specification and the appended claims, it is to be understood that the acidic material includes a liquid, gas, or solid prior to being incorporated in the mass which contains the salt complex.

In the present invention, the acidic material usually employed is an acid or a gas. The acids can include the strong or weak types, such as, for example, hydrochloric, sulphuric, nitric, carbonic, acetic acids, whereas the gas is for the most part an anhydride of an acid or an "acid anhydride gas".

The large number and variety of acidic materials can be best illustrated by the following specific examples, viz. HCl , SO_2 , SO_3 , CO_2 , air, NO_2 , H_2S , N_2O_5 , PCl_5 , SOCl_2 , ClO_2 , H_2Se , BF_3 , CS_2 , COS .

From the above examples of compounds and classes of compounds which can be used as acidic materials, it should be understood that all of them are not equivalent for this invention, because under certain conditions some are more desirable or effective than others.

Generally, the complex formed is prepared by heating the components, at a superatmospheric temperature while insuring thorough mixing and then further heating said mixture to substantially remove all free water or alcohol, including water of hydration which may be present. The following methods illustrate the manner by which the complex can be formed, namely:—

- (a) The compound AH or the salt thereof, is added to the oil-soluble salt of an acidic organic compound, followed by addition of an aqueous solution or suspension the salt or base thereto. The mixture is held at a superatmospheric temperature for a reasonable length of time while insuring thorough mixing, and then the total mixture is further heated to substantially remove all free water or alcohol including water of hydration which may be present.
- (b) The salt or base in a dry state is added to a mixture of oil-soluble acidic organic compound or salt thereof, the compound AH or the salt thereof and either water, alcohol, or mixtures of alcohols or water and alcohol; heated to a superatmospheric temperature while insuring thorough mixing and then further heated to remove substantially all free water or alcohol including water of hydration which may be present;
- (c) The acidic organic compound is mixed with the compound AH or the salt thereof, then an aqueous solution or suspension or an alcoholic solution or suspension of the salt or base is added thereto. The mixture is heated and agitated at a superatmospheric temperature for a time sufficient to insure thorough mixing and followed by subjecting the total mixture to dehydration conditions in order to remove substantially all free water or alcohol including water of hydration which may be present.
- (d) A mixture of the oil-soluble acidic organic compound or the salt thereof, the compound AH or the salt thereof, and the salt or base is heated and agitated at a superatmospheric temperature for a time sufficient to insure thorough mixing, and followed by heating the total mixture in order to remove substantially

all free water or water of hydration which may be present;

- 6 (e) The sediment when formed from any of the aforementioned methods can be employed either alone or with an additional amount of compound AH or the salt thereof in any of the three methods given above;
- 10 (f) In any of the methods discussed herein for preparing a salt complex, a substantial increase in cationic salt-forming radical content is effected by treating the mass with an acidic material just after substantial
- 15 amounts of water or alcohol or both, are driven off and just before the mass is filtered.

In all of the methods described above for preparing the salt complex, the step

20 of removing substantially all free water or alcohol including water of hydration which may be present is accomplished at a temperature not substantially in excess of 350° C., preferably about 110° to

25 200° C. The technique employed to remove the alcohol or water includes, for example, a conventional flash operation, heating under subatmospheric, atmos-

30 pheric, or superatmospheric pressures. It can, therefore, be seen that the temperature as well as the time for effecting the substantial removal of the alcohol of water will generally vary considerably depend on the technique employed there-

35 for. Generally, the time required to effect substantial removal of water or alcohol when employing drying other than flash techniques is about 15 minutes or less, and can be as high as 10—15 hours. Us-

40 ually, however, atmospheric pressures will be employed for such an operation, and consequently it will usually require about 1 to 5 hours to remove substantially all water or alcohol which may be present.

45 At a later stage of the process, the acidic material when used in gaseous form may be used to remove the last portion of water.

For the purposes of this specification

50 and the appended claims, the relative amounts of (1) the oil-soluble acidic organic compounds or salts thereof, and (2) the promoter is expressed as the "ratio of equivalent" of the former (1)

55 to the latter (2). In accordance therewith, the ratio of equivalents is from about 1 to 10 to about 10 to 1, preferably from about 3 to 2 to about 7 to 2. The amount of salt or base employed in the process will be

60 sufficient to have present in the total mass at least more than about one equivalent of cationic salt-forming radicals, including those present in the oil-soluble acidic organic compound or the salt thereof and

65 the promoter, per equivalent of oil-

soluble acids organic compound or salt thereof plus the promoter.

The treatment of the salt complex with an acidic material is employed when it is desirable to lower the basic number of the

70 salt complex and/or partially or substantially recover the promoter. This treatment is effected at a temperature of about 25° to 250° C., preferably about 120 to 170° C., and by employing about 0.5 to

75 20% of acidic material based on the weight of salt complex. The time of treatment with the acidic material can vary considerably depending on the desired result. As would be expected, short

80 periods of treatment might cause only partial liberation or release of the promoter or relatively small decreases in the basic number of the salt complex; how-

85 ever, in general, periods of treatment will range from about 0.25 to 30 hours. In most cases, and particularly where it is desired to recover the promoter, the amount of acidic material used should be at least equivalent to the amount of

90 cationic salt forming radicals present as the salt of the ionizable form of promoter. When it is desired to produce a product having substantially neutral re-

95 action, the amount of acidic material used should be at least equivalent to the total cationic salt forming radicals in excess of that present as the normal salt of the oil soluble organic acid.

The metal content of the complex will

100 be defined at the ratio of the total metal in the salt complex to the amount of metal which is in the form of a normal salt of the oil-soluble acidic organic com-

105 pound. In accordance therewith the present invention includes salt complexes containing metal ratios greater than 2.2 and up to about 10 or more. As for those complexes which are treated with an

110 acidic material, it is to be noted that the metal ratio is substantially the same as in the complex prior to treating. Consequently, for acidic material treated com-

115 plexes, the same metal ratios will apply as given above. Likewise, when the salt complex is treated with an acidic material and the promoter is removed from the resultant product by distillation or other-

120 wise, it is found that the metal ratio will be substantially the same as in the salt complex before treating with the acidic material.

It is convenient, as a means of designating the amount of overbasing to

125 employ the ratio of total metal salt-forming radicals in the salt complex to the amount of metal salt-forming radicals which are in the form of a normal salt of the oil-soluble acidic organic compound. Hereinafter, this ratio will be referred to

130

as the "metal salt-forming radical ratio". In accordance therewith, the metal salt-forming radical ratio of the salt complex will be in the same range as given hereinabove for the metal ratio.

It has been found that the salt complex can be prepared by using small quantities of water, alcohol, or mixtures of both, such as about 1 mole of same per mole of salt or base which is employed as the basing agent. However, more usually about 5 to 50 moles of water, alcohol or mixtures of both per mole of salt or base used, and preferably about 15 to 30 moles per mole.

To substantially increase the metal content of the salt complex, the total mass is treated with an acidic material just prior to filtering same to separate the desired salt complex. This treatment is effected at a temperature of about 25° to 250° C. preferably about 120° to 170° C., using about 0.5 to 20% of acidic material, based on the total mass, and for a period of about 0.25 to 30 hours. Treatment with an acid anhydride gas may be accelerated by superatmospheric pressure.

In order to better understand the present invention, the following specific examples thereof are given; however it should be understood that no undue limitations or restrictions should be imposed by reason thereof.

The following examples give the preparation of a plurality of products which range in cationic salt forming radical content from about that of the normal salt up to many times that amount.

In certain of the specific working examples given hereafter, reference is made in certain instances to complexes prepared by "conventional techniques". These examples are illustrative of prior art techniques and are given solely to provide a basis for comparison with the products of the present invention. These "conventional techniques", it will be noted, do not employ the promoter of the present invention.

We have found that sulphate ash and/or metal content values, and the metal ratio values calculated therefrom, are one

of the most reliable means for characterizing certain of the salt complexes. As the description of the invention proceeds, it will become apparent that the neutralization number of a salt complex is in certain instances an unreliable index of the amount of excess metal salt forming radicals in such complex, since it is greatly affected by the type of basing agent employed and can be varied within wide limits without significantly changing the metal salt forming radical content of the product by treatment of the mass with air, CO₂, or the like.

The above is not to be construed as a statement that the neutralization number is not an important property of a salt complex. For some uses, for example in lubricants, it is advantageous in certain instances to employ a salt complex of a substantially neutral character, whereas in other instances a salt complex of high alkalinity has been found to produce the desired results.

EXAMPLE 1

1000 grams of the barium salt of unsaturated paraffin wax sulphonic acid containing 13.1% sulphate ash were mixed with 455 grams of a mineral oil having a viscosity of 160 SSU at 100° F. and 109.5 grams of para-tertiary-butyl phenol (ratio of equivalents is 1.54), placed in a suitable vessel and heated to about 95° C. with stirring. To this mixture was added a slurry of barium oxide (containing 269 grams of barium oxide and 920 grams of water), and the total mixture was heated at about 100° C. for one hour. The temperature was slowly raised to about 150° C. and held there for about one hour until substantially all of the water was removed. Then about 3% Hyflo (Registered Trade Mark) (a filter-aid) was added to the product to facilitate filtering. The salt complex was then separated from the product by filtration. The salt complex thus prepared had the following properties:—

Basic No.	-	-	-	53.8
% sulphate ash	-	-	-	26.5
Metal ratio	-	-	-	2.49

SOLUBILITY

	Solvent	% of product added	Initial appearance	Appearance after 1 week	Appearance after 1 month
105	Pa. 150 neutral oil	50	Clear	Clear	Clear
	" " " "	10	"	"	"
110	" " " "	1	"	"	"

The salt complex product was fluid, brown in colour and did not contain any odor.

The unsaturated paraffin wax substituted of the sulphonic acid is produced by first chlorinating a saturated paraffin wax and then dehydro-chlorinating this product to produce a compound commonly referred to in the United States of unsaturated paraffin wax or paraffin wax unsaturated.

The preparation given in Example 1 is a typical illustration of the present invention. In Example 2 given below, a basic sulphonate was prepared in accordance with a conventional technique for comparison with the product given in Example 1.

EXAMPLE 2

511 grams of the barium salt of unsaturated paraffin wax sulphonic acid given in Example 1 were mixed with 75 grams of water and heated to about 60° C. with stirring. 58 grams of barium oxide were added to the mixture, which was then heated to about 150° C. and held there for one hour until substantially all of the water was removed. The product was filtered with the aid of Hyflo (Registered Trade Mark) in order to separate the complex salt. The salt complex had the following properties:—

Basic No.	- - -	16.2
% sulphate ash	- - -	19.7
Metal ratio	- - -	1.63

The salt was a waxy solid, brown in color, and did not contain any odor.

EXAMPLE 3

1000 grams of the barium salt of mono-paraffin wax substituted naphthalene sulphonic acid containing 8.63% sulphate ash were mixed with 445 grams of mineral oil having a viscosity of 160 SSU at 100° F. and 64.5 grams of para-tertiary-butyl phenol (ratio of equivalents is 1.7) and heated to about 90° C. A slurry of barium oxide (203.5 grams of barium oxide and 543 grams of water) was added, and the mixture was heated for two hours at the reflux temperature, and then dehydrated at about 165° C. for a period of one hour. Hyflo (Registered Trade Mark) was then added to the product and the salt complex was recovered by filtration. The salt complex had the following properties:—

Basic No.	- - -	44.1
% sulphate ash	- - -	17.9
Metal ratio	- - -	2.39

The salt complex prepared in accordance with Example 3 was compared with a product which was made by a conventional technique, as shown in Example 4 below.

EXAMPLE 4

1000 grams of the barium salt of mono-paraffin wax substituted naphthalene sulphonic acid given in Example 3 were heated to about 95° C. and barium oxide slurry (115 grams barium oxide and 100 grams water) was added to the mixture. The total mixture was held at a temperature of 100° C. for about one hour, and then dehydrated at a temperature of about 150° C. for about one hour. The salt complex was separated by filtering the product. Throughout the above preparation a nitrogen atmosphere was maintained above the reaction mixture. The resultant salt complex was liquid and black in color. The following properties were determined for the product:—

Basic No.	- - -	18.9
% sulphate ash	- - -	12.2
Metal ratio	- - -	1.45

EXAMPLE 5

400 grams of the barium salt of mono-paraffin wax substituted naphthalene sulphonic acid disulphide containing 8.2% sulphate ash and 27 grams of para-tertiary-butyl phenol were placed in a suitable vessel and heated to 90° C. (ratio of equivalents is 1.54). A barium oxide slurry constituting 66.5 grams of barium oxide and 180 cc. of water was added to the mixture and refluxed for about one hour. The temperature was then slowly raised to about 160° C. over a period of about four hours and held at that level for about 1.5 hours until substantially all of the water was removed. The salt complex was separated by filtering. The product was a viscous liquid, black in color, and contained a very slight odor. The following properties were determined for the salt complex:—

Basic No.	- - -	69.7
% sulphate ash	- - -	24.3
Metal ratio	- - -	3.50

The product obtained in accordance with Example 5 was then compared with a salt complex obtained under a conventional technique as shown in Example 6 below.

EXAMPLE 6

20 ml. of water were added to 450 grams of the barium salt of mono-paraffin wax substituted naphthalene sulphonic acid disulphide given in Example 5 and heated to a temperature of about 60° C. 27.5 grams of barium oxide were then added to the mixture and the temperature was slowly raised to about 160—170° C. and held there for about one hour until substantially all of the water was removed. The salt complex was then separated by filtration. The product was fluid in consistency, black in color, and contained a

slight odor. The following properties were determined for the product:—

Basic No.	- - -	5.27
% sulphate ash	- - -	8.75
Metal ratio	- - -	1.10

- 5 It is to be noted that the barium salt of mono-paraffin wax substituted naphthalene sulphonic acid disulphide has a sulphate ash of about 8.2% and that the complex formed by the conventional technique did not increase the sulphate ash content appreciably. However, as shown in Example 5, the method of the present invention produces a complex containing substantially more metal in combination.

- 15 Other types of oil-soluble organic acids or salts thereof were combined in accordance with the method of the present invention. In the following examples, it is to be noted that in every instance a salt complex was formed containing more metal than is possible by known techniques.

EXAMPLE 7

- 25 6000 grams of a 30% by weight oil solution of barium petroleum sulphonate (sulphate ash content 7.6%) were mixed with 348 grams of para-tertiary-butyl phenol in a 12-liter, 3-neck flask (ratio of equivalents 1.7) and heated to 95° C. A slurry of barium oxide constituting 1100 grams of barium oxide and 2911 grams of water was then added and the mixture held there for about one hour at a temperature of about 90—95° C. The total mixture was then slowly raised in temperature to 150° C. and dehydrated at that temperature over a period of about 4½ hours. The salt complex was separated by filtration and was found to be a slightly viscous liquid, black in color, and did not contain any odor. The properties of the salt complex were as follows:—

Basic No.	- - -	76.0
% barium	- - -	20.0
% sulphate ash	- - -	34.0
Metal ratio	- - -	3.65

EXAMPLE 10

- 90 777 grams of di-(2-ethylhexyl) dithiophosphoric acid, 308 grams of iso-nonyl phenol (ratio of equivalents 1.52) and 914 grams of solvent extracted mid-continent oil having a viscosity of 160 SUS @ 100° F. were mixed together, followed by an addition of BaO slurry consisting of 773 grams of BaO and 2060 cc. of H₂O,

Basic No.	- - -	78.0
% barium	- - -	22.7
% sulphate ash	- - -	38.6
Metal ratio	- - -	4.52

EXAMPLE 11

- 110 172 grams of di-(n-hexyl) dithiophos-

Basic No.	- - -	72.1	
% sulphate ash	- - -	23.1	45
Metal ratio	- - -	3.59	

EXAMPLE 8

- 620 grams of di-(2-ethyl-hexyl) monothiophosphoric acid, 310 grams of iso-nonyl phenol (ratio of equivalents is 1.52) 50 755 grams of mineral oil having 160 SUS @ 100° F., and 2060 ml. of water were mixed together. Then 774 grams of BaO were added over a half hour period. The total mixture was then refluxed for one hour at 100° C., whereupon the temperature was raised to 150° C., and held at that level for one hour. The temperature of the mixture was allowed to cool to 50—60° C., and then blown with CO₂ to obtain a neutral product. The complex obtained had the following properties:—

Acid No.	- - -	6.85
% barium	- - -	17.2
Metal ratio	- - -	2.65

65

EXAMPLE 9

- 405 grams of di-(2-ethyl hexyl) dithiophosphoric acid, 99 grams of para-tertiary-butyl phenol (ratio of equivalents 1.52) and 473 grams of solvent extracted 70 mid-continent oil having a viscosity of 160 SUS @ 100° F. were mixed together and heated to 50° C. A slurry comprising 387 grams of BaO and 1030 cc. of water was added quickly, maintaining the temperature at about 65° C. The mixture was then heated to 100° C. and held there for one hour. Then the temperature was raised to 150° C. over a period of 2½ hours and held there for one hour. The product 80 was obtained by filtering the mass and was found to be a slightly viscous liquid, red in color, and contained a slight odor. The following properties were determined for the product:—

85

(calculated from metal content)

- while keeping the temperature below 65° C. The total mixture was then heated at 100° C. for 1 hour, followed by a rise in temperature to 150° C. over a period of 2½ hours, and maintained at that level for 1 hour. The desired product was a slightly viscous liquid, red in color, and contained a slight odor. The product had the following properties.

(calculated from metal content)

- phoric acid, 500 grams of petroleum sulphonic acid, 159 grams of iso-nonyl 115

phenol (ratio of equivalents of oil soluble acids to iso-nonyl phenol is 1.52), and 1170 cc. of water were mixed together, then 437 grams of BaO were added over a period of $\frac{1}{2}$ hour. The mixture was heated at reflux temperature for 1 hour, fol-

	Basic No.	-	-	-	-	87.1
	% barium	-	-	-	-	28.6
15	% sulphate ash	-	-	-	-	48.8
	Metal ratio	-	-	-	-	5.22

EXAMPLE 12

172 grams of di-(n-hexyl) dithiophosphoric acid, 500 grams of petroleum sulphonic acid and 98 grams of para-tertiary-butyl phenol (ratio of equivalents of oil soluble acids to para-tertiary-butyl phenol is 1.52) were mixed together. To this mixture was added a slurry of 387

	Basic No.	-	-	-	-	121
	% barium	-	-	-	-	30.05
35	% sulphate ash	-	-	-	-	51.0
	Metal ratio	-	-	-	-	5.36

EXAMPLE 13

249 grams of petroleum naphthenic acid, 88.6 grams of para-tertiary butyl phenol (ratio of equivalents is 1.70, 1212 grams of conventionally refined mid-continent oil having a viscosity of 110 SUS @ 100° F., 347 grams of BaO and 700 ml. of H₂O were placed in a 5 liter 3 neck flask and heated to 100° C., while stirring. The mixture was maintained at 100°—105° C. for about 1 hour; thereafter the temperature was raised to 150°—160° C. and held at that level for 1 hour. Following the one hour heating period at 150°—160° C., the mixture was blown with CO₂ for about $\frac{3}{4}$ hour at about the same temperature level. The mass was then filtered with the aid of Hyflo (Registered Trade Mark) and the separated product had the following properties:—

	Basic No.	-	-	-	-	1.98
	% sulphate ash	-	-	-	-	25.10
	Metal ratio	-	-	-	-	4.10

A mixture of different oil-soluble metal sulphonates was treated in accordance with a conventional technique and by the method of the present invention to determine what effect if any the two types of sulphonates would have on the quality of the product. Such preparations are given in Examples 14 and 15 below.

EXAMPLE 14

A mixture containing 500 grams of the barium salt of petrolatum sulphonic acid (sulphate ash 9.2%), 197 grams of the barium salt of petroleum sulphonic acid (sulphate ash 7.6%), and 50 grams of para-tertiary-butyl phenol (ratio of equivalents of the sulphonates to promoter is 1.54) was heated to 95° C. a slurry of

lowed by heating to 150° C. over a period of $2\frac{1}{2}$ hours, and then maintaining that temperature for 1 hour. The desired product was a viscous liquid, brown in color, and contained a slight odor. The following properties were determined:—

(calculated from metal content)

grams of BaO and 1080 cc. of water. The mixture was heated at 100° C. for 1 hour, and then the temperature was raised to 150° C. and held at that level for 1 hour. The product was a highly viscous liquid, brown in color, and contained a slight odor. The following properties of the product were determined:—

(calculated from metal content)

barium oxide constituting 123 grams of barium oxide and 330 grams of water was added to the mixture. The total mixture was refluxed for one hour at 100° C. and then the temperature was slowly raised to 150° C. for a period of one hour to substantially remove all the water. The complex was separated by filtration and was found to be a liquid, and black in color. The following properties were determined:—

	Basic No.	-	-	-	-	27.7
	% sulphate ash	-	-	-	-	17.25
	Metal ratio	-	-	-	-	2.41

EXAMPLE 15

By the conventional technique, 480 grams of the barium salt of petrolatum sulphonic acid and 200 grams of the barium salt of petroleum sulphonic acid of Example 14 were mixed with a barium oxide slurry containing 68 grams of water and 60.8 grams of barium oxide. The components were heated to a temperature of 160° C. for one hour until substantially all the water was removed. The complex was separated by filtration and was found to a viscous liquid, light brown in color, and contained a slight odor. The following properties were determined:—

	Basic No.	-	-	-	-	20.2
	% sulphate ash	-	-	-	-	11.72
	Metal ratio	-	-	-	-	1.51

While most of the examples given herein use either a neutral or normal salt of the organic acid as a starting material to produce the high metal content complex, nevertheless it is contemplated for the purposes of this invention to employ the complexes produced by conventional tech-

niques as a starting material. The following example illustrates this concept:--

EXAMPLE 16

1634 grams of a barium petroleum sulphonate—BaO complex (obtained by dehydrating a barium petroleum sulphonate, 7.6% sulphate ash, water and BaO mixture at 150° C. for 1 hour, and producing a complex which has a basic number of 40, metal ratio of 2.25 and a 16% sulphate ash) and 121 grams of diisobutyl phenol (ratio of equivalents 1.7) were combined and heated to 70° C. To this mixture were added 665 cc. of water. followed by a slow addition of 175 grams of BaO. The entire mixture was then refluxed for 1 hour, and the temperature was raised to 150° C. over a 3 hour period and held there for 1 hour. Prior to filtering, the mass was blown with CO₂ at a rate of 3.6 cubic foot/hr. for 1½ hours at 150° C. The product analyzed as follows:—

	Basic No. - - - -	8.67
25	% sulphate ash - - -	24.8
	Metal ratio - - - -	4.13

It can be seen from the sulphate ash analyses of the product and overbased sulphonate used as a starting material that there was an increase from 16.0 to 24.8 in sulphate ash. Clearly, therefore, the conventionally overbased materials can be used as starting materials in the present invention.

Other experiments were conducted in order to determine the effect of a higher dehydration temperature in the preparation of the salt complex of the present invention. In this respect, Examples 17 and 18 below illustrate the effect of higher temperatures.

EXAMPLE 17

2000 grams of a 30% oil solution of barium petroleum sulphonate (sulphate ash 7.6%) were mixed with 120 grams of paratertiary-butyl phenol (1.52 ratio of equivalents) and heated to 95° C. To said mixture was added a slurry of barium oxide containing 520 grams of barium oxide and 1390 ml. of water. The total mixture was heated for one hour at 100° C., and then was slowly raised in temperature over a period of three hours to 200° C. The mixture was maintained at this high temperature for a period of one-half hour. The salt complex was separated by filtering and was found to be an oily liquid, reddish-brown in color, and contained a faint odor. The following properties were determined:—

60	Basic No. - - - -	71.5
	% sulphate ash - - -	24.3
	Metal ratio - - - -	3.80

EXAMPLE 18

2035 grams of 30% oil solution of barium petroleum sulphonate (sulphate ash 7.6%) were mixed with 74.5 grams of phenol (1.67 ratio of equivalents) and heated to 100° C. A barium oxide slurry containing 483 grams of barium oxide and 1290 ml. of water was added and the mixture refluxed slowly for a period of one hour at 100° C. The mixture was then dehydrated by heating slowly to 200° C. and maintaining such a temperature for a period of about one-half hour. The salt complex was separated by filtration and was found to be an oily liquid, reddish-brown in color, and contained a slight odor. The following properties were determined for the complex:—

	Basic No. - - - -	111.5
	% sulphate ash - - -	32.8
	Metal ratio - - - -	5.56

In addition to the promoters tested above, various other types were tried to determine the effectiveness thereof in forming salt complexes.

EXAMPLE 19

A mixture of 2280 grams of a 30% oil solution of barium petroleum sulphonate (sulphate ash 7.6%) and 83 grams of phenol (ratio of equivalents is 1.53) was heated to a temperature of 60° C. 496 grams of barium oxide and 1300 grams of water were added to the above mixture and the temperature was raised to 90—100° C. After holding at said temperature for one hour, the temperature was raised over a period of three hours to 150° C. and held at that level for ½ hour. The resultant salt complex was fluid in consistency and dark red in color. The following properties were determined:—

	Basic No. - - - -	91.4
	% sulphate ash - - -	26.8
	Metal ratio - - - -	4.37

EXAMPLE 20

1500 grams of a 30% oil solution of barium petroleum sulphonate having a sulfate ash of 7.6%, 93 grams of isopropyl phenol (ratio of equivalents 1.7), and 670 grams of water were placed in a 3-liter flask and heated to 60° C. 250 grams of BaO were then added, and the temperature was allowed to rise to 100° C. The mixture was held at 100° C. for 1 hour, followed by a rise in temperature to 150° C. over a 2 hour period, where the temperature was held for ½ hour. The total mixture was filtered, and the filtered product had the following properties:—

	Basic No. - - - -	87.8
	% sulphate ash - - -	25.95
	Metal ratio - - - -	3.88

EXAMPLE 21

1140 grams of a 30% oil solution of barium petroleum sulphonate having a sulphate ash of 7.6% and 80 grams of para-tertiary-amyl phenol (ratio of equivalents 1.54) were heated to 70° C. Thereafter 600 cc. of water were added, followed by a slow addition of 227 grams of BaO. The mixture was refluxed for 1 hour, and then the temperature was raised to 160° C. over a period of 4 hours and held there for $\frac{1}{2}$ hour. The product was separated by filtration, and had the following analyses:—

15	Basic No. - - - -	85.5
	% sulphate ash - - -	24.60
	Metal ratio - - - -	3.96

EXAMPLE 22

2583 grams of a 30% oil solution of barium petroleum sulphonate having a 7.6% sulphate ash, 144.2 grams of betanaphthol (ratio of equivalents is 1.69 and 1262 ml. of water were combined and mixed thoroughly. Then 472 grams of BaO were added over a 1 hour period, followed by maintaining the total mixture at 100° C. for 1 hour. The temperature was then raised to 150° C. and held there for 1 hour. Prior to filtering the mixture, it was blown with CO₂ for 75 minutes at which time the mixture had a basic number of 0.8. After filtering, the product analyzed as follows:—

35	Basic No. - - - -	4.88
	% sulphate ash - - -	23.8
	Metal ratio - - - -	3.90

EXAMPLE 23

1530 grams of a 30% oil solution of barium petroleum sulphonate (7.6% sulphate ash), 739 grams of a product obtained by reacting 4 moles of turpentine with 1 mole of P₂S₅ at 140° (ratio of equivalents 1.7) and 740 ml. of water were mixed together. 272 grams of BaO were then added slowly followed by increasing the temperature of the mixture to 90—100° C.; after holding the temperature at that level for 1 hour, it was again increased to 150° C. and held there for 1 hour to remove substantially all of the water. Prior to filtering the mass, it was blown with CO₂ for 15 minutes at 120°—130° C. to produce a slightly acid mass. The complex was separated by filtration and it had the following properties:—

55	Acid No. - - - -	1.22
	% barium - - - -	11.25
	Metal ratio - - - -	4.30

EXAMPLE 24

60 1530 grams of a 30% solution of barium petroleum sulphonate having a 7.6% sulphate ash, 129 grams of iso-nonyl phenol

(ratio of equivalents is 1.7) and 727 ml. of water were combined and thoroughly mixed. Then 271 grams of BaO were added and the total mixture was held at 100° C. for 1 hour. The temperature was then raised to 150—160° C. and held there for 1 hour. Prior to filtering, the mass was blown at about 150° C. with CO₂ until a basic number of about 1 was obtained. The filtered product analyzed was as follows:—

	Basic No. - - - -	3.9	
	% sulphate ash - - -	25.0	75
	Metal ratio - - - -	4.17	

EXAMPLE 25

2600 grams of a 30% oil solution of barium petroleum sulphonate having a 7.6 sulphate ash, 215 grams of tertiary-butyl chlorophenol (ratio of equivalents is 1.7) and 1265 cc. of water were combined, followed by an addition of 459 grams of BaO. The temperature of the total mixture was raised to 100° C. and held there for 1 hour. Then the temperature was raised to 150° C. where it was held for 1 hour. Prior to filtering the mixture, it was blown for 3 hours with CO₂ at 135—145° C. until the mixture was slightly basic. The filtered product analyzed as follows:—

	Basic No. - - - -	13.3	
	% sulphate ash - - -	25.45	
	Metal ratio - - - -	4.38	95

EXAMPLE 26

1530 grams of a 30% oil solution of barium petroleum sulphonate having a 7.6% sulphate ash and 210 grams of trichlorodiphenyl ether sulphonic acid (ratio of equivalents is 1.7) were heated to 70° C. To this mixture were added 725 grams of water, followed by the addition of 271 grams of BaO. The entire mixture was refluxed for 1 hour, then heated to 150° C. over a 3 hour period and held there for 1 hour. Prior to filtering, the mixture was blown with CO₂ at 150° C. and at a rate of 3.6 cu. ft./hr. for 1½ hours. The filtered product analyzed as follows:—

	Acid No. - - - -	0.45	111
	% sulphate ash - - -	24.7	
	Metal ratio - - - -	4.34	

EXAMPLE 27

1530 grams of a 30% oil solution of barium petroleum sulphonate having a 7.6% sulphate ash and 175 grams of tertiary-butyl naphthalene sulphonic acid (ratio of equivalents is 1.7) were combined and heated to 70° C. To this mixture were added 725 grams of H₂O, followed by a slow addition of 271 grams of BaO. The entire mixture was then refluxed for one hour, and then heated to 150° C. over

a 3 hour period. The mixture was held at 150° C. for 1 hour. Prior to filtering, the mass was blown at 150° C. with CO₂ at a rate of 3.6 cu.ft./hr. for 1½ hours. The

5 filtered product analyzed as follows:—

Acid No.	-	-	-	-	0.41
% sulphate ash	-	-	-	-	24.1
Metal ratio	-	-	-	-	4.12

EXAMPLE 28

10 1530 grams of a 30% oil solution of barium petroleum sulphonate having a 7.6% sulphate ash and 131 grams of methyl naphthalene sulphonic acid (ratio of equivalents is 1.7) were added to the

15 mixture, followed by a slow addition of 271 grams of BaO. The entire mixture was refluxed for 1 hour, then the temperature was raised to 150° C. over a three

20 hour period, and held there for 1 hour. Prior to filtering, the mass was blown with CO₂ at a rate of 3.6 cu.ft./hr. for 1½ hours at 150° C. The filtered product analyzed as follows:—

Basic No.	-	-	-	-	Nil
% sulphate ash	-	-	-	-	25.9
Metal ratio	-	-	-	-	4.41

EXAMPLE 29

1530 grams of a 30% oil solution of barium petroleum sulphonate having a

80 7.6% sulphate ash, 113 grams of diisobutenyl sulphonic acid (ratio of equivalents is 1.7) and 725 grams of H₂O were combined and heated to 70° C. To this mixture were added 271 grams of BaO.

85 and the entire mixture was heated at 100° C. for 1 hour. The mixture was then heated at 150° C. for one hour, followed by blowing with CO₂ at 150° C. prior to filtering, to obtain a substantially neutral

40 mass. The filtered product analyzed as follows:—

Basic No.	-	-	-	-	0.23
% sulphate ash	-	-	-	-	24.6
Metal ratio	-	-	-	-	4.10

EXAMPLE 30

45 Di-isopropyl benzene sulphonic acid obtained by reacting 162 grams of di-isopropyl benzene with 122 grams of chlorosulphonic acid for 1 hour at 100° C. were

50 combined with 2600 grams of a 30% oil solution of barium petroleum sulphonate having a 7.6% sulphate ash and 1220 ml. of water. The ratio of equivalents of oil soluble sulphonate to sulphonic acid is 1.7.

55 Then 461 grams of BaO were added slowly and the mixture held at 100° C. for 1 hour. The temperature was raised to 150° C. and held there for 1 hour. Prior to filtering, the mixture was blown with CO₂ for ½

hour at 120—140° C. The filtered product analyzed as follows:—

Acid No.	-	-	-	-	1.22
% sulphate ash	-	-	-	-	25.4
Metal ratio	-	-	-	-	4.33

EXAMPLE 31

Cymene sulphonic acid obtained by reacting 134 grams of cymene with 122 grams of chlorosulphonic acid at 70—100° C. for 1½ hours was combined with 2600

70 grams of a 30% oil solution of barium petroleum sulphonate having a 7.6% sulphate ash and 1220 ml. of water. The ratio of equivalents of oil soluble sulphonate to sulphonic acid is 1.7. To this mixture were added 461 grams of BaO,

75 and the entire mixture was then held at 85—100° C. for 1 hour. Then the temperature was raised to 150° C. and held there for 1 hour. Prior to filtering, the mass was blown with CO₂ for ½ hour at 130° C. The filtered product analyzed as follows:—

Acid No.	-	-	-	-	0.95
% sulphate ash	-	-	-	-	25.8
Metal ratio	-	-	-	-	4.38

EXAMPLE 32

2600 grams of a 30% oil solution of barium petroleum sulphonate having a 7.6% sulphate ash, 2219 grams of tertiarybutyl dichlorophenol (ratio of equivalents is 1.7) and 1265 grams of water were combined, followed by an addition of 459

90 grams of BaO over a 45 minute period. The entire mixture was held at 100° C. for 1 hour, followed by maintaining the temperature at 150° C. for 1 hour. Prior to filtering, the mass was blown with CO₂ for 90 minutes at 135—150° C. until the reaction mass was slightly acidic. The filtered product analyzed as follows:—

Bais No.	-	-	-	-	6.45
% sulphate ash	-	-	-	-	23.2
Metal ratio	-	-	-	-	3.85

EXAMPLE 33

2600 grams of a 30% oil solution of

105 barium petroleum sulphonate having a 7.6% sulphate ash, 236 grams of di-isopropyl dithiophosphoric acid (ratio of equivalents is 1.7) and 1220 ml. of water were combined, followed by a slow addition

110 of 461 grams of BaO. The mixture was held at 100° C. for 1 hour, and then heated to 150° C. and held there for 1 hour. Prior to filtering, the mass was blown with CO₂ for 20 minutes at 125—

115 150° C. The filtered product analyzed as follows:—

Acid No.	-	-	-	-	-	0.27
% barium	-	-	-	-	-	14.25
% sulphate ash	-	-	-	-	-	24.2 (calculated from metal content)
Metal ratio	-	-	-	-	-	4.15

5

EXAMPLE 34

2600 grams of a 30% oil solution of barium petroleum sulphonate having a 7.6 sulphate ash, 100 grams of acetyl-acetone (ratio of equivalents is 1.7) and 1265 cc. of water were combined, followed by a slow addition of 459 grams of BaO over a 1 hour period. The entire mixture was held at 94° C. for 1 hour, followed by a 1 hour period of heating at 150° C. Prior to filtering, the mass was blown with CO₂ for 1 hour at 135—150° C. The filtered product analyzed as follows:—

Acid No.	-	-	-	-	0.2
% sulphate ash	-	-	-	-	22.8
Metal ratio	-	-	-	-	3.48

20

EXAMPLE 35

1530 grams of a 30% oil solution of barium petroleum sulphonate having a 7.6% sulphate ash and 206 grams of di-iso-butyl naphthalene sulphonic acid (ratio of equivalents is 1.7) were combined and heated to 70° C. 725 grams of water were then added, followed by a slow addition of 271 grams of BaO. The mixture was refluxed for 1 hour, and then held at 150° C. for 1 hour. Prior to filtering, the

Acid No.	-	-	-	-	-	0.12
% barium	-	-	-	-	-	23.2
% sulphate ash	-	-	-	-	-	3.2 (calculated from barium content)
Metal ratio	-	-	-	-	-	3.6

60

The salt complex can also be prepared by starting with the oil-soluble sulphonic acid and treating with the promoter and the basing agent. This technique differs from those given above because as shown in all the above examples, the normal metal sulphonate or conveniently over-based sulphonate was employed as a starting material. In order to demonstrate that the metal ratio of the salt complex obtained by this method is greater than by conventional techniques, a comparison was made with a conventional technique in which the acid was employed as a starting material. In this respect, Examples 37 and 38 below are illustrative.

EXAMPLE 37

The oil-soluble petroleum sulphonic acid employed in this test was derived by combining a 60% oil solution of sodium petroleum sulphonate with the stoichiometric amount of sulfuric acid (96% strength) at a temperature of 60—70° C. for a period of two hours. After allowing the mixture to stand about 12 hours,

80

85 strength) at a temperature of 60—70° C. for a period of two hours. After allowing the mixture to stand about 12 hours,

mixture was blown with CO₂ at a rate of 3.6 cu.ft/hr. for 1.25 hours at a temperature of 150° C. The filtered product analyzed as follows:—

Acid No.	-	-	-	-	0.24
% sulphate ash	-	-	-	-	23.6
Metal ratio	-	-	-	-	4.12

The following example illustrates the use of an inorganic promotor.

40

EXAMPLE 36

135 grams of fluoboric acid (HBF₄) were added to 1530 grams of a 30% oil solution of barium petroleum sulphonate having a 7.6% sulphate ash. 725 ml. of H₂O were added followed by an addition of 271 grams of BaO, and the temperature was raised to 100—105° C. and held there for one hour. Thereafter the temperature was raised to 150° C. and CO₂ was blown through the mixture until the mass was slightly acidic. The CO₂ treatment was discontinued and the temperature was held at 150—160° C. for about 1 hour. The mass was then filtered with the aid of "Hyflo" (Registered Trade Mark), and the separated product has the following properties:—

it was filtered twice through a glass cloth. 2375 grams of the product just described were combined with 205.7 grams of para-tertiary-butyl phenol, (ratio of equivalents is 1.39), 1647 grams of a low-viscosity mineral oil having a viscosity of about 120 SUS at 100° F., 927.6 grams of barium oxide and 2480 grams of water and heated for one hour at a temperature of 98° C. The mixture was then dehydrated for one hour at a temperature of 150° C. so as to remove substantially all of the water. The product was a viscous liquid, brown in color, and contained a mild odor. The following properties were determined for the desired product:—

Basic No.	-	-	-	-	74.2
% sulphate ash	-	-	-	-	24.4
Metal ratio	-	-	-	-	4.02

105

EXAMPLE 38

500 grams of the oil-soluble petroleum sulphonic acid given in Example 37 above were heated to 75° C. 55 grams of water were then added and followed by a slow addition of 162.2 grams of barium oxide.

110

The total mixture was maintained at a temperature of 150° C. for a period of one hour. The desired complex was separated by filtration and was found to be a very viscous liquid, black in color, and did not contain any odor. The following properties were determined for the product:—

	Basic No. - - - -	53.7	
10	% sulphate ash - - -	25.65	
	Metal ratio - - - -	1.74	

The salt complexes of the present invention can be prepared by first adding water to the mixture of the oil-soluble metal sulphionate or sulphonic acid and promoter, and then adding the basing agent in a dry state. In this respect, Example 39 given below illustrates an alternative method by which the salt complex can be prepared.

EXAMPLE 39

1000 grams of the barium salt of di-paraffin wax substituted phenol sulphonic acid (sulphate ash 6.6%) were admixed with 55 grams of para-tertiary-butyl phenol (ratio of equivalents is 1.54) and heated to a temperature of 90° C. 800 cc. of water were then added. The mixture was mixed thoroughly and then 300 grams of dry barium oxide were added. The total mixture was refluxed for two hours followed by an addition of 573 grams of a mineral oil having a viscosity of 160 SSU at 100° F. The temperature was raised over a period of four hours to 170° C. and then maintained there one hour. The salt complex was obtained by filtering the product and was found to be a viscous liquid, dark brown in color, and contained a faint odor. The following properties were determined for the salt complex:—

	Basic No. - - - -	67.8	
	% sulphate ash - - -	23.8	
45	Metal ratio - - - -	2.67	

Another experiment was performed in which the salt of the ionizable form of promoter was employed. Example 40 below illustrates this feature of the invention.

EXAMPLE 40

1700 grams of a 30% oil solution of barium petroleum sulphionate (sulphate ash 7.6%) were admixed with 105 grams of barium phenate (ratio of equivalents is 1.70) and 570 grams of water. The mixture was heated to 75–100° C. whereupon 214 grams of barium oxide were added. The temperature of the mixture was maintained at 100° C. for one hour and then raised slowly to 150° C. and held at this level for a period of one hour. The salt complex was then separated from the reaction product by filtration and was found to be a viscous liquid, light brown in

color, and contained a slight odor. The following properties were determined for the salt complex:—

	Basic No. - - - -	68	
	% sulphate ash - - -	21.4	70
	Metal ratio - - - -	2.23	

The following examples by comparison illustrate the substantial increase in metal content of the complex which is obtained by treating the mass with an acidic material before filtering to separate the desired product.

EXAMPLE 41

1700 grams of a 30% oil solution of barium petroleum sulphionate having a sulphate ash of 7.6% were mixed with 134 grams of diisobutyl-phenol (ratio of equivalents is 1.7) and heated to 70° C. 302 grams of BaO and 800 cc. of water were added thereto, and the mixture was refluxed for 1 hour. The temperature was then raised to 160° C. over a period of 6 hours and maintained at that temperature for one hour. The mass was filtered and the product obtained was a liquid, brown in color, and contained a slight odor. The following properties of the product were determined:—

	Basic No. - - - -	66	
	% sulphate ash - - -	22.2	95
	Metal ratio - - - -	3.64	

EXAMPLE 42

1700 grams of a 30% oil solution of barium petroleum sulphionate having a sulphate ash of 7.6% were mixed with 134 grams of diisobutyl-phenol (ratio of equivalents is 1.7) and heated to 70° C. Then 800 cc. of H₂O and 302 grams of BaO were added and the mixture refluxed for 1 hour. The temperature was raised to 150° C. and maintained there for one hour. CO₂ was then injected therethrough at 150° C. and at a rate of 1,650 cc./min. for 38 minutes. The mass was then cooled and filtered to separate the complex. The product was liquid, brown in color, and contained a faint odor. The following properties of the product were determined:—

	Basic No. - - - -	5.05	115
	% sulphate ash - - -	26.0	
	Metal ratio - - - -	4.52	

EXAMPLE 43

400 lbs. of a 30% oil solution of barium petroleum sulphionate having a sulphate ash of 7.6% were heated to 80° C., and 32.5 lbs. of diisobutyl-phenol (ratio of equivalents is 1.67) were added thereto. Then 197 lbs. of water were added to the mixture, with stirring to insure thorough mixing. 73 lbs. of BaO were added thereto over a 30 minute period at 55–80° C. The mixture was agitated for

about 10 minutes more at 80° C. then the temperature was raised to 100° C. and held there for 1 hour. Thereafter, the temperature was raised to about 150° C. and maintained at that level for 1 hour. Following this step, CO₂ was blown through the mass until about 75 lbs. thereof had been used over a period of 3 hours and at a temperature of 135—170° C. The mass was then filtered and the complex was found to have the following properties:—

Basic No.	-	-	-	5.0
% sulphate ash	-	-	-	25.7
Metal ratio	-	-	-	4.35

EXAMPLE 44

4590 grams of a 30% oil solution of

	Product A	Product B
Basic No.	63	4.5
% sulphate ash	19.5	29.5
Metal ratio	3.18	5.35

From the foregoing examples it is shown that the method of treating the mass prior to filtering with an acidic material results in substantial increases in sulphate ash of the complex, and thus correspondingly higher metal ratios.

The salt complexes can also be prepared by combining oil-soluble metal sulphonate and the basing agent in the presence of the sediment which may form. The following examples illustrate the utility of the sediment for preparing salt complexes of the present invention.

EXAMPLE 45

1700 grams of a 30% oil solution of barium petroleum sulphonate having a 7.6% sulphate ash were mixed with 61 grams of phenol (ratio of equivalents is 1.70) and the mixture was heated to 75° C. 261 grams of barium oxide and 710 grams of water were then added and the total mixture was raised in temperature to 100° C. and held at that level for one hour. Thereafter, the temperature was raised slowly to 150° C. and held there for about one hour. The total mixture was allowed to settle overnight, followed by decantation and filtering. In this experiment 450 grams of sediment were produced. The filtered salt complex was a viscous liquid, light brown in color, and contained a slight odor. The following properties of the product were determined:—

Basic No.	-	-	-	59.5
% sulphate ash	-	-	-	21.2
Metal ratio	-	-	-	3.20

The sediment obtained in Example 45 was employed in the preparation of a salt complex in the method given in the following Example No. 46.

barium petroleum sulphonate having a 7.6% sulphate ash, 363 grams of diisobutyl-phenol (ratio of equivalents is 1.7) and 2,800 grams of H₂O were heated to 60° C. 1,042 grams of BaO were added slowly and then the temperature of the mixture was raised to 94—98° C. and held there for 1 hour. Thereafter the temperature was raised to 150° C. in 4 hours, and maintained there for 1 hour. A small portion of the mass, 361 grams, was removed and filtered to give product A, whereas the remainder (5,296 grams) was blown with SO₂ at 170° C. until 330 grams thereof was used. This latter mass was then filtered and the product given below as product B was obtained. The analyses of products A and B are as follows:—

EXAMPLE 46

1700 grams of a 30% oil solution of barium petroleum sulphonate having a 7.6% sulphate ash, 20 grams of phenol, 450 grams of sediment obtained from the preparation given in Example 45. 710 grams of water and 261 grams of barium oxide (barium oxide added slowly) were mixed together and heated to a temperature of 100° C. for about one hour. The total mixture was then raised in temperature in a slow manner to about 150—160° C. and held there for one hour until substantially all the water was removed. The salt complex was separated by filtration and was found to be a viscous liquid, light brown in color, and contained a slight odor. The following properties were determined for the salt complex:—

Basic No.	-	-	-	82.6
% sulphate ash	-	-	-	26.4

In the following examples, the basing agent and the salt of the acidic organic compound contains a metal other than barium.

EXAMPLE 47

A mixture of 45.9 grams of phenol, 244 grams of water and 90.5 grams of Ca(OH)₂ was stirred at reflux temperature for two hours. Thereafter 1046 grams of a 45% oil solution of calcium petroleum sulphonate having a 6.7% sulfate ash (ratio of equivalents is 0.41) were added. The temperature of the mixture was then raised to 125° C., at which level substantially all of the water was removed. Prior to filtering the mixture, it was blown with CO₂ for three hours at a temperature of about 120—150° C. The complex was fluid, brown in color and did not contain any odor. The complex had the following analyses:—

Basic No.	- - - -	8.07
% sulphate ash	- - - -	18.35
Metal ratio	- - - -	3.07

EXAMPLE 48

5 1046 grams of a 45% oil solution of calcium petroleum sulphonate (6.7% sulphate ash) and 228 grams of phenol (ratio of equivalents is 0.41) were mixed together. The mixture was heated to 100° C. whereupon 124 grams of calcium methoxide were added while stirring the mixture. The temperature of the total mixture was held at 100—120° C. for two hours while insuring thorough mixing, and then 22 grams of water were added. The total mixture was then agitated for 1 hour while holding the temperature at 105° C. The temperature of the mixture was then raised and at about 120° C., CO₂ was injected into the mixture and heating continued until the entire mixture had been held at 150° C. for 1 hour to remove substantially all of the water. The complex was obtained by filtration and had the following properties:—

Basic No.	- - - -	9.3
% sulphate ash	- - - -	17.9
Metal ratio	- - - -	2.94

Another preparation was made in which dissimilar metals were present in the organic acid compound and the basing agent. The following example illustrates this feature of the invention:—

EXAMPLE 49

85 1793 grams of a 45% oil solution of calcium petroleum sulphonate, having a 6.45% sulfate ash, 206 grams of octyl phenol (ratio of equivalents 1.7) and 954 grams of water were mixed together. Then 358 grams of BaO were added, and the mixture was agitated thoroughly. While insuring thorough mixing the temperature was raised to 90—100° C. for one hour. Thereafter, the temperature was raised to 150° C. over a two hour period and held at that level for one hour. The complex obtained by filtering the mixture had the following properties:—

Basic No.	- - - -	4.2
% sulphate ash	- - - -	25.2
Metal ratio	- - - -	3.94

The complexes of this invention can be also obtained by using a mixture of oil soluble organic acid and the salt thereof.

85 The following example illustrates this concept:—

EXAMPLE 50

80 2875 grams of petroleum sulphonic acid and 6000 grams of a 30% oil solution of barium petroleum sulphonate (sulphate ash is 7.6%) were mixed with 553.7 grams of para-tertiary butyl phenol (ratio of equivalents is 1.60). The mixture was

heated to about 50° C. whereupon a slurry of BaO (consisting of 2027.6 grams of BaO and 5395 grams of water) was added and the mixture was then maintained at a temperature of about 90—95° C. for an additional hour. Upon inspection the mixture appeared thoroughly mixed, therefore the temperature was slowly raised to 150° C. and held there for approximately one hour. The product analyzed as follows:—

Basic No.	- - - -	73.0
% sulphate ash	- - - -	23.3
Metal ratio	- - - -	3.73

The following examples illustrate the preparation of salt complexes wherein the ratio of equivalents falls outside of said preferred range, but comes within the broad range found to be operable:—

EXAMPLE 51

1000 grams of a 30% oil solution of barium petroleum sulphonate containing 7.6% sulphate ash were mixed with 750 grams of water at 50° C. 282 grams of BaO were added thereto, followed by the addition of a slurry consisting of 460 grams of water, 87 grams of BaO, and 115 grams of para-tertiary-butyl phenol (ratio of equivalents of sulphonate to phenolic compound is 0.77). The mass was stirred for ½ hour at about 100° C., then it was heated to 200° C. and maintained at that temperature for 2 hours.

The salt complex was separated by filtration. It was a red-brown, viscous liquid, and the following properties:—

Basic No.	- - - -	46
% sulphate ash	- - - -	27.9
Metal ratio	- - - -	5.4

Another preparation was made in which the components were combined in the presence of a mixture of alcohol and water. The following example illustrates this concept:—

EXAMPLE 52

1700 grams of a 30% oil solution of barium petroleum sulphonate (7.6% sulphate ash). 98 grams of para-tertiary-butyl phenol (ratio of equivalents is 1.7), 500 ml. of water and 300 ml. of methanol were mixed at atmospheric temperature. 302 grams of BaO were then added while stirring the mixture, followed by an increase in temperature to 100° C. The mixture was agitated while holding the temperature at 90—100° C. for 1 hour. Thereafter the temperature was increased to 150—155° C. and held there for 1 hour to remove substantially all of the water. The complex was separated by filtration and had the following analyses:—

Basic No.	- - - -	78.7
% sulphate ash	- - - -	26.2
Metal ratio	- - - -	4.25

In another pair of experiments, a com-

parison was made between the process of the present invention and a conventional process, when using duplicate amounts of components. It is clearly evident from the following examples that this invention will give substantially better results with respect to metal concentration of the complex than is obtainable by the conventional technique.

10 EXAMPLE 53

1530 grams of a 30% oil solution of barium petroleum sulphonate having a 7.6% sulphate ash, 88 grams of para-tertiary-butyl phenol (ratio of equivalents is 1.7), 271 grams of BaO and 725 ml. of water were mixed together at 60–70° C. The temperature of the mixture was raised to 100–105° C. and held there for one hour while insuring thorough mixing. Thereafter the temperature was raised to 150–160° C., and held at that level to remove substantially all the water. The complex was separated by filtration and had the following analyses:—

25	Basic No. - - - -	85.2
	% sulphate ash - - -	25.5
	Metal ratio - - - -	4.12

This may be compared with the following example employing conventional technique:—

EXAMPLE 54

1530 grams of a 30% oil solution of barium petroleum sulphonate having a 7.6% sulphate ash were mixed with 725 ml. of water at about 60° C. Then 271 grams of BaO were added. The temperature of the mixture was raised to 100–105° C. and held there for one hour while insuring thorough mixing. Thereafter the temperature was raised to 150–160° C. and held there for one hour to substantially remove all the water. The complex was separated by filtration and had the following properties:—

45	Basic No. - - - -	36.0
	% sulphate ash - - -	15.34
	Metal ratio - - - -	2.14

From the foregoing it will be noted that by following the process of the present invention, two types of complexes may be produced, both of which are different from any produced by any of the prior art processes. The first form of such complex is the immediate product with the promoter included therein in chemical combination. The second form of novel product is that which results from the treatment of the complex just described with an acidic material which has the effect, as stated above, of liberating the promoter from the complex without any substantial change in the cationic salt forming radical ratio of the complex. The liberation of the promoter by this step

of treating the first-named complex with an acidic material may be followed by a recovery, as by distillation, of the promoter thus liberated, leaving the complex substantially free of the promoter material. A third product which is probably different from each of the two named above may be produced by treating the complex initially formed with an acidic material prior to the removal by filtration of the excess basing agent. When following this latter procedure, the promoter material is permitted to remain in the complex, and when this procedure is followed it has been found that unusually high cationic salt forming radical ratios may be secured in the ultimate product.

As previously indicated, the immediate product formed by the use of the promoter material may be modified to recover therefrom a substantial portion of the promoter material used, by treating such immediate end product with a sufficient amount of an acidic material which in the presence of the mass will form a material having a higher ionization constant than the promoter. After a portion of the promoter material has been thus regenerated by treating the immediate product with an acidic material, the regenerated promoter may then be separated therefrom by any one of the several known means, or the regenerated promoter material may be left in the mass and the latter then treated with an additional amount of a salt-forming material, and it will be found that the concentration of the stably-held cationic radicals can be further increased.

The following are examples of such further steps in our process:—

EXAMPLE 55

The salt complex produced in Example 39 was mixed with 1239 grams of mineral oil and heated to a temperature of 190° C. While maintaining this temperature for a period of 1½ hours, CO₂ was blown through the mixture. The temperature was then lowered to 150° C., the passage of CO₂ through the mixture was continued and the basic number of the mixture was tested every 10 minutes, until the analysis showed a basic number of 2.5. The salt complex—CO₂ product was then separated and was found to be liquid in consistency, brown in color, and contained a very slight odor. The following properties were determined for the product:—

	Basic No. - - - -	2.5
	% sulphate ash - - -	23.2

By comparison, the product of Example 39 contained a sulphate ash of 23.8% whereas this same product after blowing with CO₂ contained a sulphate ash of 23.2. Therefore, it can be seen that the metal

ratio of the salt complex is substantially the same after treatment with CO₂.

EXAMPLE 56

6043 grams of the salt complex prepared in accordance with Example 7 were placed in a suitable vessel and CO₂ gas was injected at the bottom of the vessel at a rate of 3750 cc. per minute for a period of 1 1/2 hours. During this period, the temperature was in the range of 30–70° C. At the end of the blowing operation the product weighed 6346 grams, showing a gain in weight of 303 grams. The product was fluid, dark red in color, and contained no odor. The following properties were determined for the salt complex-CO₂ product:—

Basic No.	- - - - -	4.3
% sulphate ash	- - - - -	22.7

It can be seen, therefore, by the gain in weight of the product that the CO₂ actually enters into combination with the salt complex. Furthermore, the metal ratio of the product is substantially the same as the salt complex prior to being blown with CO₂, since the sulphate ash content is substantially the same as before CO₂ treatment.

EXAMPLE 57

1288 grams of the salt complex prepared in accordance with the method of Example 3 was blown with CO₂ at a temperature of 30–50° C. until the product showed an acid reaction. Following this CO₂ treatment, the product was blown with nitrogen for a period of 15 minutes. The product thus produced was very viscous, reddish-brown in color, and did not contain any odor. The following properties were determined:—

Acid No.	- - - - -	5.36
% sulphate ash	- - - - -	17.94

The above examples clearly show that it is possible to treat the salt complex with an acid anhydride gas and obtain a product which is definitely acid. Furthermore, treatment with an acid-anhydride gas to such extent does not change the metal ratio of the salt complex, since the sulphate ash content is substantially the same as before treatment.

Another salt complex product which was blown with CO₂ is given in Example 58 below.

EXAMPLE 58

2500 grams of a 30% oil solution of barium petroleum sulphonate containing 7.6% sulphate ash were mixed with 45.6 grams of phenol, (ratio of equivalents is 3.36) and heated to 95° C. A slurry of barium oxide containing 422 grams of barium oxide and 1125 ml. of water was added to the mixture, with stirring, and held at a temperature of 97–102° C. for

a period of one hour. The temperature was then slowly raised over a period of three hours to 150° C. and maintained at that level for an additional period of one hour until substantially all the water was removed. The desired salt complex was separated by filtering and was found to be an oily liquid, brown in color, and contained a faint odor. The following properties were determined:—

Basic No.	- - - - -	60.6
% sulphate ash	- - - - -	22.3
Metal ratio	- - - - -	3.34

EXAMPLE 59

1250 grams of the salt complex produced in accordance with the method given in Example 58 above were blown with CO₂ for approximately two hours at a temperature below 60° C., until an acid number of 5.0 was obtained. The weight of product obtained was 1260 grams.

The CO₂-salt complex product was then heated at a temperature of 190° C. under a vacuum of 10 mm. producing a distillate weighing about 10 grams. The distillate was then dissolved in iso-propyl ether and then dried over magnesium sulphate, filtered and then the magnesium sulphate was removed by filtration. 5 grams of residue remained. This residue was found to be phenol, thus indicating that treatment of the salt complex with an acidic material liberates at least a portion of the promoter from complex formation.

After the distillation step, the following properties for the salt complex were determined:—

Basic No.	- - - - -	2.96
% sulphate ash	- - - - -	22.4

The percent sulphate ash of the CO₂-salt complex product indicates that little or no metal is removed from the complex as a result of the CO₂ treatment and the distillation step to recover the promoter.

EXAMPLE 60

1440 grams of the salt complex obtained by the method given in Example 45, was blown with CO₂ for about two hours at a temperature of 30–60° C. until the product showed an acid number of 6. The product thus obtained was then heated at a temperature of 200° C. under vacuum of 4 mm. to recover approximately 15 grams of phenol. The residue of the distillation was a viscous liquid, light brown in color, and contained a slight odor. This product possessed the following properties:—

Basic No.	- - - - -	1.06
% sulphate ash	- - - - -	22.6

Here again it is shown that the treatment of the salt complex with an acidic

material liberates the promoter from complex formation in the salt. On a quantitative basis, it was determined that approximately $\frac{1}{3}$ of the original phenol was still held in complex formation in the CO_2 -treated product.

The salt complex prepared in accordance with Example 61 below was treated with SO_2 as shown in Example 62 which is given below.

EXAMPLE 61

6000 grams of a 30% solution of barium petroleum sulphonate (sulphate ash 7.6%), 348 grams of para-tertiary-butyl phenol, (ratio of equivalents is 1.70) and 2915 grams of water were mixed and heated to a temperature of 60°C . 1100 grams of barium oxide were added slowly and the temperature of the total mixture was raised to $94-98^\circ\text{C}$. and held there for one hour. The temperature of the mixture was then slowly raised over a period of 7½ hours to about 150°C . and held at that level for an additional hour until substantially all the water was removed. The salt complex obtained is a liquid, brown in color, and did not contain any odor. The following properties were determined:—

Basic No.	-	-	-	82.5
% sulphate ash	-	-	-	26.0
Metal ratio	-	-	-	4.2

EXAMPLE 62

6623 grams of the product produced in accordance with Example 61 were treated with SO_2 at $25-50^\circ\text{C}$. until 327 grams of the gas were combined with the salt complex. The product thus obtained had a neutralization number or a basic number of 0. The SO_2 -salt complex product was liquid, brown in color, and did not contain any odor.

An experiment was conducted in order to determine whether air which contains CO_2 would be effective as an acidic material. The examples below illustrate the utility of air for this purpose.

EXAMPLE 63

380 lbs. of a 30% oil solution of barium petroleum sulphonate were mixed with 21.9 lbs. of para-tertiary-butyl phenol (ratio of equivalents is 1.7) and 184 lbs. of water. This mixture was heated to 50°C . and 68 lbs. of BaO were added over a period of $1\frac{1}{2}$ hours while not permitting the temperature to go above 65°C . The total mixture was held at 100°C . for one hour, then heated to 150°C . over a period of 4.8 hours and held there for one hour. The desired product was fluid, dark red, and possessed the following properties:—

Basic No.	-	-	-	80.5
% sulphate ash	-	-	-	26.0
Metal ratio	-	-	-	4.2

EXAMPLE 64

6000 grams of the product produced in Example 63 were placed into a 12-liter, 3-necked flask and heated to 175°C . The mass was then blown with air until a basic number of 1 was obtained. The final product contained a sulphate ash of 26.4% indicating substantially no change in the amount of metal present.

EXAMPLE 65

To a mixture of 166 grams (0.25 equivalents) of petroleum sulfonic acid, 98 grams of mineral lubricating oil and 20 ml. of water heated at 70°C ., was added 10.5 grams (0.25 equivalents) of lithium hydroxide monohydrate and the resulting mixture was heated at reflux temperature for 30 minutes. The hot solution was treated with 31 grams (0.15 equivalents) of diisobutylphenol and an additional 41.0 grams (0.98 equivalents) of lithium hydroxide monohydrate, then heated at reflux temperature for one hour, and dried at 150°C . Carbon dioxide was bubbled through the hot mixture for 45 minutes, and then the mixture was dried again at 150°C . for 30 minutes, treated with a siliceous filter aid and filtered. The filtrate was a brown, free-flowing liquid, having the following properties:—

% sulphate ash	-	-	-	19.5
Metal ratio	-	-	-	4.6
Basic number	-	-	-	21.3

EXAMPLE 66

A mixture of 665 grams (1.0 equivalent) of sodium petroleum sulfonate, 425 grams of mineral lubricating oil, 124 grams (0.60 equivalents) of diisobutylphenol and 332 grams (4.15 equivalents) of 50% aqueous sodium hydroxide was heated at reflux temperature for one hour and then was dried at $150-160^\circ\text{C}$. for three hours. Carbon dioxide was bubbled through the mixture for one hour, and the mixture was dried again at 150°C . for 30 minutes, then treated with a siliceous filter aid and filtered. The filtrate was a brown, free-flowing liquid, having the following properties:—

% sulphate ash	-	-	-	15.0
Metal ratio	-	-	-	3.0
Basic number	-	-	-	2.1

EXAMPLE 67

To a solution of 140 grams (1.18 equivalents) of nickel chloride hexahydrate in 200 grams of water was added a solution of 82 grams (1.46 equivalents) of potassium hydroxide in 82 grams of water, and the resulting green precipitate was collected on a filter. It was added to a mixture of 470 grams (0.33 equivalents) of nickel petroleum sulfonate and 40.3

grams (0.196 equivalents) of diisobutylphenol and the whole was heated with 100 ml. of water at reflux temperature for one hour, then dried at 150° C. The dried mixture was treated with carbon dioxide at 150—160° C. for one hour, treated with a siliceous filter aid and filtered. The filtrate was a light green, viscous liquid having the following properties:—

10	% metal - - - -	6.94
	Metal ratio - - - -	4.2

EXAMPLE 68

To a solution of 164 grams (1.08 equivalents) of ferrous sulfate in 100 ml. of water there was added 73 grams of ammonium hydroxide (29%) and the resulting blue precipitate was collected on a filter and added to a mixture of 434 grams (0.33 equivalents) of ferrous petroleum sulfonate, 40.3 grams (0.196 equivalents) of diisobutylphenol and 100 grams of water. This mixture was heated at reflux temperature for one hour, treated with 100 grams of mineral lubricating oil, and dried at 150° C. Carbon dioxide was bubbled through the mixture for 90 minutes at 150—160° C., the mixture was treated with a siliceous filter aid and filtered. The filtrate was a dark brown, viscous liquid which has the following properties:—

% metal - - - -	3.7
Metal ratio - - - -	2.6

EXAMPLE 69

To an aqueous solution of 77 grams (0.59 equivalent) of chromic sulfate was added 37 grams (0.30 equivalent) of ammonium hydroxide (29%) and the resulting precipitate isolated by filtration. This precipitate was added to a mixture of 200 grams (0.17 equivalents) of chromic petroleum sulfonate and 20 grams (0.10 equivalent) of diisobutylphenol and heated at reflux temperature for one hour, then dried at 150° C. The product was a green liquid and was shown by analysis to have a chromium content of 0.5%.

EXAMPLE 70

555 grams of a 40% oil solution of barium petroleum sulfonate (10% sulfate ash content), 17.4 grams of acetamide (ratio of equivalents of sulfonate to promoter is 1.7), 100 grams of a low-viscosity solvent-extracted mid-continent oil, and 58 grams of water were stirred together at 70° C. and then 135.5 grams of BaO were added. The whole was heated for 1 hour at 100°—110° C. and 1 hour at about 150° C. Thereafter CO₂ was blown into the mass at 150° C. until a substantially neutral titre was obtained (about 0.5 hour required). Added 15 grams of

nonyl alcohol to the process mass and filtered to separate the desired metal complex (the filtrate), which was a moderately viscous, brown, oil-soluble, liquid having the following analysis:—

Basic No. - - - -	3.7	
% sulphate ash - - - -	21.2	
Metal ratio - - - -	2.77	70

EXAMPLE 71

555 grams of a 40% oil solution of barium petroleum sulphonate (10% sulphate ash content), 38 grams of ethyl acetoacetate (ratio of equivalents of sulphate to promoter is 1.7) and 60 grams of water stirred together at 70° C. and then 135.5 grams of BaO were added. The whole was heated at 100°—110° C., and 300 grams of a low-viscosity, solvent-extracted mid-continent oil were added. The temperature was then raised to 150° C. and CO₂ was blown through the mass for about 2 hours. 35 grams of nonyl alcohol were added and the mass was filtered to isolate the desired metal complex (the filtrate), which was a moderately viscous, brown, oil-soluble liquid having the following analysis:—

Acid No. - - - -	0.5	90
% sulphate ash - - - -	22.3	
Metal ratio - - - -	3.72	

EXAMPLE 72

6000 grams of 30% oil solution of barium petroleum sulphonate (sulphate ash 7.6), 348 grams of para-tertiary-butyl phenol (ratio of equivalents is 1.53) and 2911 grams of water were mixed and heated to a temperature of 60° C. To this mixture was slowly added 100 grams of barium oxide and the temperature was then raised to 94—98° C. and held there for a period of one hour. The total mixture was raised in temperature to 150° C. over a period of seven and one-half hours and held there for a period of one hour. The metal complex was separated by filtering the product. The complex was found to be a lubricant, brown in color, and did not contain any odor.

The following properties were determined for the product:—

Basic No. - - - -	72.8	
% sulphate ash - - - -	22.3	
Metal ratio - - - -	3.69	115

6190 grams of the metal complex were treated with CO₂ for a period of one-and-a-half hours at a temperature of 26 to 55° C. The product had a base number of 1.5.

1029 grams of the CO₂ metal complex were heated to 50° C. and then 109.8 grams of anhydrous barium hydroxide were added. The total mixture was held at a temperature of 100° C. for one hour and the temperature was raised to 150°

C. and held at that level for a period of one hour. The desired super-based salt was separated by filtering and was found to be fluid in consistency. The following

5 properties were determined:—

Basic No.	- - - -	31.5
% sulphate ash	- - - -	28.6
Metal ratio	- - - -	5.1

EXAMPLE 73

10 400 pounds of a 30% oil solution of barium petroleum sulphonate (sulphate ash 7.6%) were placed in a suitable vessel and heated to 26° C. At this temperature 32.5 pounds of di-isobutyl-phenol
15 were added and the mixture was mixed thoroughly. Then 197 pounds of water were added, followed by an addition of 73 pounds of BaO over a 30 minute period, while keeping the temperature 57° C. to
20 84° C. Thereafter the temperature was raised to 100° C. and kept there for one hour, followed by another temperature increase to 152° C. and maintained at the latter level also for one hour. The process mixture was then blown with 75
25 pounds of CO₂ over a three-hour period and at a temperature of 135—170° C. The separated product had the following properties:—

30 Basic No.	- - - -	5.0
% sulphate ash	- - - -	25.7
Metal ratio	- - - -	4.35

1000 grams of this product and 121.8 grams of di-isobutyl-phenol were placed in
35 a suitable container and mixed thoroughly at 50° C. Then 234 grams of B₂(OH)₂ were added, followed by raising the temperature of the mass to 100° C. and holding it there for one hour. The temperature of the mixture was again raised to
40 150° C. and maintained at that level for one hour. A portion of the process mass was filtered and the separated product analysed as follows:—

45 Basic No.	- - - -	42.8
% sulphate ash	- - - -	33.7
Metal ratio	- - - -	6.3

The remainder of the unfiltered process mass was blown with CO₂ at a rate of 3

100

	Broad range	Usual range	Preferred range
Lubricants	0.01—20%	0.2—15%	0.5—10%
Stabilizing agents for plastics	0.05—5%	0.1—3%	0.2—2%
Paint drier	0.2—25%	0.5—20%	1.0—15%

105 To better appreciate the wide variety of uses to which the salt complexes of this invention are adopted, the following specific examples are given:—

A lubricant:— % by weight

110 SAE 30 motor oil	- - - -	97.0
Product of Example 20	- - - -	2.5
Zinc di-(4-methyl-pentyl-2)-dithiophosphate	- - - -	0.5

cubic feet per hour for one hour at 150° 50 C. The process mass was then filtered and the desired superbased salt had the following properties:—

Basic No.	- - - -	7.6
% sulphate ash	- - - -	39.8
Metal ratio	- - - -	9.3

In all of the above examples the mahogany soaps are referred to as metal petroleum sulphonate, and likewise the mahogany acid is designated as petroleum
60 sulphonic acid.

Having thus described the present invention by furnishing specific examples thereof, it is to be understood that no undue limitations or restrictions are to be
65 imposed by reason thereof, but that the scope of the invention is defined by the appended claims.

The salt complexes produced in accordance with the present invention can be employed in lubricants including oils and greases, and for such purposes as in crank-cases, transmissions, gears, etc. as well as in torque converter oils. Other suitable
70 uses for such complexes are in asphalt emulsions, insecticidal compositions, fireproofing and stabilizing agents in plasticizers and plastics, paint driers rust inhibiting compositions, pesticides, forming compositions, cutting oils,
75 metal drawing compositions, flushing oils, textile treatment compositions, tanning compositions, metal cleaning compositions, emulsifying agents, antiseptic cleansing compositions, penetrating agents, gum solvent compositions, fat splitting agents, bonding agents for ceramics and asbestos, asphalt improving agents, flotation agents, improving agents for hydrocarbon fuels such as e.g. gasoline and fuel oil, etc.

More particularly, the complexes of this invention are especially adopted for the preparation of lubricants, paint driers and plastics, especially the halogen bearing
95 ing plastics. In these respects the salt complex can be employed in the following concentrations based upon the weight of the total composition:—

	Broad range	Usual range	Preferred range
A stabilizing agent in a plastic:—			
Polyvinyl chloride	- - - -	60.0	
Diocetyl phthalate	- - - -	39.0	
Product of Example 49	- - - -	1.0	

A stabilizing agent in a plastic:—

	% by weight	110
Polyvinyl chloride	- - - -	60.0
Diocetyl phthalate	- - - -	39.0
Product of Example 49	- - - -	1.0

A paint drier:—

Lead-base housepaint	- - - -	94.0
Product of Example 48	- - - -	6.0

120

Other modes of applying the principle of the invention may be employed, change being made as regards the details described, provided the features stated in any 5 of the following claims be employed:—

What we claim is:—

1. A method of preparing oil-soluble organic basic salts or soaps having a metal ratio as hereinbefore defined greater than 10 2.2, in which an oil-soluble organic acid (or salt thereof) and an excess amount of basing agent of the kind described are reacted together in the presence of water and/or a water-soluble alcohol or alcohols 15 and a promoter of the kind described which is a phenolic compound for the purpose of increasing the metal salt-forming radical ratio, the ratio of equivalents of oil-soluble organic acid (or salt thereof) 20 to equivalents of said promoter being in the range from about 1:10 to about 10:1 and the amount of basing agent being such that there is present in the reaction mass a total of substantially more than 25 one equivalent of metal salt-forming radicals, including those present in the oil-soluble organic acid (or salt thereof) and in the promoter, per equivalent of oil-soluble organic acid plus promoter, and 30 the reaction mass is maintained at a temperature and for a period of time sufficient to drive off substantially all free water, water of hydration and/or alcohol which may be present, and form the 35 organic metal complex.
2. A method of preparing oil-soluble organic basic salts or soaps having a metal ratio as hereinbefore defined greater than 2.2, in which an oil-soluble organic acid 40 (or salt thereof) and an excess amount of basing agent of the kind described are reacted together in the presence of water and/or a water-soluble alcohol or alcohol and a promoter of the kind described for 45 the purpose of increasing the metal salt-forming radical ratio, the ratio of equivalents of oil-soluble organic acid (or salt thereof) to equivalents of said promoter being in the range from about 1:10 to 50 about 10:1 and the amount of basing

agent being such that there is present in the reaction mass a total of substantially more than one equivalent of metal salt-forming radicals, including those present in the oil-soluble organic acid (or salt 55 thereof) and in the promoter, per equivalent of oil-soluble organic acid plus promoter, and the reaction mass is maintained at a temperature and for a period of time sufficient to drive off substantially 60 all free water, water of hydration and/or alcohol which may be present, and form the organic metal complex, and said organic metal complex is treated with an acidic material. 65

3. A method as claimed in Claim 1, in which the product is treated with an acidic material for the purpose of liberating therefrom at least a portion of the promoter. 70

4. A method as claimed in Claim 2 or 3, in which at least a part of the promoter is left in the resultant product.

5. A method as claimed in Claim 4, in which the resultant product is treated with 75 an additional amount of salt-forming material.

6. A method as claimed in any of the preceding claims in which the acid (or salt thereof) is an oil-soluble sulphonic acid 80 (or salt thereof).

7. A method as claimed in any of the preceding claims in which the basing agent is an alkaline earth metal oxide or hydroxide. 85

8. A method as claimed in Claim 2 or 3, in which the acidic material is carbon dioxide.

9. A method as claimed in any of the preceding claims in which the process is 90 carried out in the presence of a hydrocarbon oil.

10. A method as claimed in any of the preceding claims, substantially as described with reference to any of the 95 examples given, with the exception of those examples which are given to illustrate the technique of the prior art.

MARKS & CLERK.

THIS PAGE BLANK (USPTO)